CHEMICAL REACTIVITY OF URANIUM TRIOXIDE POLYMORPHS IN REDUCTION BY HYDROGEN*

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Summary

The α, β, γ and amorphous polymorphs of uranium trioxide have been prepared and their reactivity towards reduction to UO_2 and further conversion to UF_4 studied. The UO_3 polymorphs are characterized by X-ray, porosity measurements and density determinations. Reduction of UO_3 to UO_2 was carried out by differential thermal analysis and the results of the DTA experiments were analysed in terms of the reactivity of the UO_3 sample. The reactivity of the product UO_2 towards hydrofluorination was measured by its oxygen content upon reoxidation after two weeks of air exposure. The ratio O:U depends upon the UO_3 polymorph concerned and the temperature of reduction to UO_2.

1. Introduction

Current methods for the preparation of UF_4 include the calcination of uranyl nitrate hexahydrate (UNH) or ammonium uranate to UO_3, followed by the reduction of UO_3 to UO_2 and subsequent hydrofluorination of UO_2 to UF_4. Studies of the conversion of UO_3 to UF_4 show that the reactivity of intermediate UO_2 towards hydrofluorination is related to the crystal structure and other physical properties of the UO_3 precursor. Moreover, the properties of UO_3 (structure type, surface area and density) are strongly influenced by the method of preparation, including starting materials, precipitation conditions and thermal treatment [1]. Kinetic studies on the reduction of UO_3 to UO_2 by hydrogen [2] and calcination–reduction studies on ammonium diuranate (ADU) have been reported [3]. Differential thermal analysis (DTA) in air and subsequent thermogravimetric reduction have been

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performed on UO_3 polymorphs [4, 5]. However, comparative DTA in hydrogen of the various forms of UO_3 has not been reported.

In this work, three polymorphs of UO_3 (α, β and γ) and the amorphous form were prepared by thermal decomposition of UNH or its derivatives. UNH is usually the starting material in commercial methods for the preparation of UF_4. The trioxides were characterized by X-ray, density and surface area measurements. Reduction to UO_2 was carried out by DTA in a flow of hydrogen and the results of the DTA experiments were analysed in terms of the reactivity of the UO_3 sample. The reactivity of the UO_2 product was estimated from the O:U ratio.

2. Experimental details

2.1. Preparation of UO_3 (α, β, γ and amorphous)

A large number of methods have been reported [5 - 9]. α-UO_3 was prepared using two different routes of synthesis: (i) from uranium peroxide ($UO_4.2H_2O$) obtained according to Cordfunke [10] and Watt *et al.* [11] (designated $\alpha(1)$ (from UNH 99%) and $\alpha(2)$ (from UNH with a purity of better than 98%)) (Table 1); (ii) by thermal decomposition of UNH, heated slowly from room temperature to 500 °C, sintered for 12 h and rapidly cooled (designated $\alpha(3)$). Five samples of β-UO_3 were prepared from ammonium diuranate (ADU), precipitated at pH values ranging from 7 to 10 and sintered at 400 °C. To synthesize γ-UO_3, UNH was heated slowly to 500 °C and then cooled in the furnace to room temperature [12, 13]. For amorphous (A) UO_3, the starting material was the dihydrate $UO_3.2H_2O$ which was heated to 400 °C and cooled in the furnace [8, 9]. The apparent O:U ratios of the polymorphs (see Section 2.2) lie between 3.02 and 3.26 (Table 1), the highest values being observed for the β phases. This implies the presence of impurities: NO_3^- for α, γ and A and NO_3^- and $NH4^+$ for β-UO_3. The lowest values were found for $\alpha(3)$, $\gamma(1)$ and $\gamma(2)$, prepared by direct thermal decomposition of UNH.

2.2. Analysis

Phases were identified by X-ray powder diffraction with a Philips diffractometer. The oxygen contents of the UO_3 samples before and after hydrogen reduction were determined thermogravimetrically by heating the samples for 1 h at 750 °C; the O:U ratio was deduced therefrom. Densities were measured pycnometrically at room temperature and were calculated from the difference in weight of the material in air and in carbon tetrachloride. Prior to analysis and density measurements, the UO_3 samples were outgassed under vacuum at 120 °C for 1 h.

2.3. Apparatus and procedures

Differential thermal analysis (DTA) was performed in hydrogen in an induction furnace controlled by electronic regulation. The heating rate was

TABLE 1

Properties and DTA results of the prepared UO_3 oxides

Type	*pH of precipitation*	*O:U ratio*	*Calculated density*	*Measured density*	*ADU SA* ($m^2 g^{-1}$)	*UO_3 SA* ($m^2 g^{-1}$)	*DTA peaks*[a] (°C)		$(O:U)_1$	$(O:U)_2$
α(1)	—	3.08	8.41	7.29	—	8.49	491(w)	572(m)	2.16	2.22
α(2)	—	3.11	8.36	7.05	—	6.38	516(w)	571(s)	2.11	2.18
α(3)	—	3.00	8.42	7.13	—	2.98	—	590(m)	2.13	2.20
β(1)	7	3.15	8.34	6.35	14.87	23.39	530(m)	566(m)	2.24	2.34
β(2)	8	3.18	8.40	6.26	16.08	24.05	499(m)	551(m)	2.25	2.44
β(3)	8	3.24	8.19	6.05	16.08	25.53	505(w)	552(m)	2.24	2.43
β(4)	10	3.20	8.39	6.14	17.57	26.19	484(m)	554(m)	2.30	2.43
β(5)	10	3.26	8.30	6.01	17.57	27.77	498(s)	548(s)	2.27	2.44
γ(1)	—	3.02	7.98	7.55	—	2.39	548(m)	614(s)	2.09	2.15
γ(2)	—	3.04	8.03	7.40	—	2.82	545(m)	600(m)	2.12	2.16
Amorphous	—	3.15	—	5.82	—	5.05	534(s)	579(m)	2.21	2.31

[a]Intensity of DTA peaks: s, strong; m, medium; w, weak;
$(O:U)_1$, ratio after DTA; $(O:U)_2$, ratio 14 days after DTA..

600 °C h^{-1} in the temperature range 25 - 700 °C. The average flow of hydrogen (500 cm^3 min^{-1}) was about three times the theoretical amount required to convert UO_3 to UO_2. The hydrogen flow was maintained while the reduction furnace was cooled to room temperature. The UO_3 polymorphs were pressed into pellets under a pressure of 400 kg cm^{-2} and were placed in a stainless steel sample holder which was introduced in a cylindrical graphite block. A Pt–Pt/Rh thermocouple was used to measure the differential temperature. The reference material was calcined alumina. Stabilization of UO_2 was achieved by rapid cooling in hydrogen to 100 °C (25 min), followed by cooling in a mixture of hydrogen and nitrogen to room temperature (for 1 h). Nitrogen was then passed through the cold reaction vessel for 30 min. The oxygen contents of the UO_2 phases were measured just after the DTA experiments and after 2 weeks of exposure to air. Brunauer–Emmett–Teller (BET) surface areas were measured with a FlowSorb 2300 analyser using the single-point method with nitrogen in helium as the absorbate. The sample was outgassed at 120 °C for 1 h and the surface area was calculated by dividing the quantity of gas that desorbed by the sample weight after desorption.

3. Results and discussion

3.1. Properties of uranium trioxides

Some of the properties of the UO_3 phases are summarized in Table 1. The measured densities are below the theoretical X-ray density for all the polymorphs. For β-UO_3, the density decreases as the ADU calcination time increases. The densities of the polymorphs decrease in the order $\gamma > \alpha > \beta >$ A. Surface area (SA) measurements show the influence of the purity of the starting UNH for α-UO_3. The SA of β-UO_3 increases with that of the ADU precursor, which increases with the pH of precipitation. The lowest values are observed for $\alpha(3)$ and γ, both resulting from direct thermal decomposition of UNH. For β-UO_3 and γ-UO_3 as the heating time increases, the SA increases. The SA values of the polymorphs increase in the order $\gamma < A < \alpha < \beta$.

3.2. Differential thermal analysis (DTA)

Results of the reduction of the UO_3 polymorphs by hydrogen are listed in Table 1. Two DTA measurements were performed on each sample. The results are identical within experimental errors. For all samples two exothermic peaks are observed, the first at temperatures ranging from 484 °C ($\beta(4)$) to 548 °C ($\gamma(1)$) and the second at temperatures ranging from 548 °C ($\beta(5)$) to 614 °C ($\gamma(1)$). For $\alpha(2)$ (prepared from less pure UNH) a third small exothermic peak is observed at 474 °C, and for β-UO_3 two weak exothermic peaks are observed between 611 and 665 °C. A small endothermic peak is observed for $\alpha(3)$, $\gamma(2)$ and A, the samples synthesized by the decomposition of UNH. The two exothermic DTA peaks observed for all the polymorphs

may be ascribed to the transition from the starting UO_3 polymorph to the intermediate U_3O_8 phase and from the U_3O_8 phase to a cubic phase. Studies on partially reduced samples [3, 14] have indicated the non-stoichiometric $UO_{2.6}$ phase as an intermediate.

As the surface area of the UO_3 polymorph increases, the DTA peaks are shifted towards lower temperatures, indicating that the stability of the UO_3 polymorphs to reduction increases in the order $\beta < \alpha < A < \gamma$. The ratio $(O:U)_1$ after DTA may be used for a qualitative comparison of the reactivity of the different polymorphs towards reduction. Values of $(O:U)_1$ range from 2.09 to 2.30; the highest values are observed for UO_2 samples obtained from the reduction of β-UO_3, which is the least stable to reduction. The oxygen content absorbed after 2 weeks in air can be estimated from the ratio $(O:U)_2$ which ranges from 2.15 to 2.44; re-oxidation is highest for β-UO_3. The reactivity of the UO_2 product, measured by the difference between $(O:U)_1$ and $(O:U)_2$, increases in the order $\gamma < \alpha < A < \beta$.

4. Conclusions

Reduction studies were performed in hydrogen on four UO_3 polymorphs using DTA in order to estimate the samples most suitable for hydrofluorination. The experiments show a relationship between the observed DTA peaks and the SA of the UO_3 sample. From the DTA results the stability of the UO_3 polymorphs towards reduction can be compared. Moreover, the reactivity of the UO_2 product can be measured from the O:U ratio after DTA.

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